

Pressure variation of the low-frequency dielectric constants of some anisotropic crystals

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The low-frequency dielectric constant for quartz, sapphire, calcite, and magnesium fluoride has been measured both parallel and perpendicular to the optic axis at several temperatures over the pressure range 0–0.3 GPa. The results, when compared with the reported values for the effect of pressure on the high-frequency dielectric constant, indicate that pressure decreases the infrared contribution to the dielectric constant for all materials except calcite. Consequently, the infrared polarizability decreases with pressure for all but calcite. Further, it is found that the infrared polarizability decreases with pressure for calcite perpendicular to the optic axis, but increases with pressure parallel to the optic axis. In addition, it is shown that the volume-independent temperature derivative of the low-frequency dielectric constant is positive for sapphire, calcite, and magnesium fluoride showing that cubic terms in the lattice potential energy dominate, while for quartz, the derivative is negative implying that quartic terms are dominant.

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I. INTRODUCTION

In a recent paper,¹ the effect of temperature on the low-frequency dielectric constant was reported for quartz, sapphire, magnesium fluoride, and calcite. This paper extends that work by reporting the effect of pressure on the dielectric constant for those materials. The combined results allow a determination of the volume-independent temperature derivative of the dielectric constant. In addition, the pressure results are considered relative to published data concerning the effect of pressure on the high-frequency dielectric constant. Those results, in conjunction with the results of the present work, allow a determination of the effects of pressure on the infrared contribution to the dielectric constant. Anomalous results are found for calcite parallel to the optic axis.

II. EXPERIMENT AND DATA REDUCTION

The samples are the same as those studied for the temperature work¹ and for the accurate determination of the 300 K dielectric constant² for all but calcite. Aluminum electrodes were evaporated onto the samples in the usual three-terminal configuration. The capacitance C and the conductance divided by the angular frequency, G/ω , were measured using a fully automated impedance bridge operating at the five audio frequencies 10^2 , $10^{2.5}$, 10^3 , $10^{3.5}$, and 10^4 Hz. The measurements were performed in the bomb described elsewhere³ and the pressures were determined using the capacitive pressure gauge also described elsewhere.⁴ The measurements were performed at several temperatures in the vicinity of room temperature, by placing the bomb in an ethylene glycol bath. In most cases, data were taken over the pressure range 0–0.3 GPa. The following equation was then fitted to the data at each temperature:

$$C_p/C_0 = 1 + aP + bP^2. \quad (1)$$

The resulting least-squares coefficients, a and b , are listed in Tables I–IV. Previous results have only been reported for calcite⁵ and sapphire.⁶ The relevant coefficients are in good agreement with the previous work.

For each material, it was assumed that the linear compressibilities could be represented by the equation

$$L_p/L_0 = 1 - dP + eP^2. \quad (2)$$

The coefficients d and e were obtained from the following

TABLE I. Coefficients in Eq. (1) for quartz.

T (K)	Comment	a (10^{-12} Pa^{-1})	b (10^{-22} Pa^{-2})
Parallel			
260	a	– 2.135	5.16
280	a	– 2.137	3.92
300	a	– 2.099	3.33
	b	– 2.087	2.84
319	a	– 2.047	3.99
	b	– 2.056	4.01
342	a	– 2.042	3.86
	b	– 2.034	3.08
Perpendicular			
300	c	7.853	1.18
	d	7.831	2.40
	e	7.574	4.10
319	c	7.781	4.46
342	c	7.765	3.62

^aValpey Z-cut, run No. 1.

^bValpey Z-cut, run No. 2.

^cValpey Y-cut, run No. 1.

^dValpey Y-cut, run No. 2.

^eValpey X-cut.

TABLE II. Coefficients in Eq. (1) for sapphire.

T (K)	Comment	a (10^{-12} Pa $^{-1}$)	b (10^{-22} Pa $^{-2}$)
Parallel			
260	a	-11.50	7.10
280	a	-11.55	4.36
300	a	-11.53	3.67
319	a	-11.74	5.69
342	a	-11.71	2.97
291	b	-10.8	-7
326	b	-11.7	3
Perpendicular			
260	a	-10.57	6.27
280	a	-10.54	2.28
300	a	-10.53	0.49
319	a	-10.64	2.43
342	a	-10.64	0.28
293	b	-10.1	-3
323	b	-10.5	0.6

^aUnion Carbide material, present work.

^bReference 6.

relations, which are appropriate for all of the crystals⁷:

$$d_{||} = s_{33} + 2s_{13}, \quad (3)$$

$$d_{\perp} = s_{11} + s_{12} + s_{13} \quad (4)$$

and

$$e_{||} = \frac{1}{2} \left(\frac{\partial s_{33}}{\partial P} + 2 \frac{\partial s_{13}}{\partial P} \right) \quad (5)$$

and

$$e_{\perp} = -\frac{1}{2} \left(\frac{\partial s_{11}}{\partial P} \Big|_T + \frac{\partial s_{12}}{\partial P} \Big|_T + \frac{\partial s_{13}}{\partial P} \Big|_T \right), \quad (6)$$

using published values for the elastic compliances and their pressure derivatives. The subscripts $||$ and \perp represent paral-

TABLE III. Coefficients in Eq. (1) for calcite.

T (K)	Comment	a (10^{-12} Pa $^{-1}$)	b (10^{-22} Pa $^{-2}$)
Parallel			
261	a	71.09	75.3
281	a	70.67	120.1
300	a	71.06	128.7
	b	70.99	139.4
319	a	71.68	129.8
342	b	72.38	132.5
Room	c	71.0	125
Perpendicular			
300	d	11.19	67
	e	11.82	43.7
Room	c	12.0	42

^aHarshaw sample No. 1.

^bHarshaw sample No. 2.

^cReference 5.

^dKarl Lambrecht sample, present work.

^eJanos optical sample, present work.

TABLE IV. Coefficients in Eq. (1) for magnesium fluoride.

T (K)	Comment	a (10^{-12} Pa $^{-1}$)	b (10^{-22} Pa $^{-2}$)
Parallel			
261	a	-21.00	13.5
280	a	-21.18	12.7
300	a	-21.35	5.1
	b	-21.24	8.08
319	a	-21.68	9.9
343	a	-21.99	13.1
Perpendicular			
261	a	-13.25	11.3
280	a	-13.40	11.2
300	a	-13.48	6.97
319	a	-13.74	10.2
342	a	-13.97	10.3

^aPreanneal.

^bPostanneal.

lel and perpendicular to the optic axis, respectively. The resultant values of the coefficients are listed in Table V.

Assuming the expression for the capacitance of a parallel-plate capacitor,

$$C = \epsilon_0 \epsilon A / l, \quad (7)$$

it follows that the zero-pressure first derivative of the dielectric constant with respect to pressure can be written as

$$\frac{1}{\epsilon_{||}} \frac{\partial \epsilon_{||}}{\partial P} \Big|_T = a_{||} - d_{||} + 2d_{\perp} \quad (8)$$

and

$$\frac{1}{\epsilon_{\perp}} \frac{\partial \epsilon_{\perp}}{\partial P} \Big|_T = a_{\perp} + d_{||}. \quad (9)$$

The values of the pressure derivatives are listed in Table VI. In addition, it follows that

TABLE V. Coefficients in Eq. (2).

Sample	Reference	d (10^{-12} Pa $^{-1}$)	e (10^{-22} Pa $^{-2}$)
Parallel			
Quartz	a	7.31	7.52
Sapphire	b	1.45	0.11
Calcite	c	8.32	0.54
Magnesium fluoride			
	d,e	3.08	0.67
Perpendicular			
Quartz	a	9.82	7.55
Sapphire	b	1.28	0.16
Calcite	c	2.75	2.28
Magnesium fluoride			
	d,e	4.24	1.37

^aH. J. McSkimin, P. Andreatch, Jr., and R. N. Thurston, J. Appl. Phys. **36**, 1624 (1965).

^bR. E. Hankey and D. E. Schuele, J. Acoust. Soc. Am. **48**, 190 (1970).

^cD. P. Dandekar, J. Appl. Phys. **39**, 3694 (1968); Phys. Rev. **172**, 873 (1968).

^dH. R. Cutler, J. J. Gibson, and K. A. McCarthy, Solid State Commun. **6**, 431 (1968).

^eG. F. Davies, Earth Plan. Sci. Lett. **34**, 300 (1977).

TABLE VI. Pressure derivative of the electronic and ionic contributions to the dielectric constant (units are 10^{-12} Pa^{-1}).

Sample	$\frac{\partial \epsilon}{\partial P} \Big _T$	$= \frac{\partial \epsilon_{el}}{\partial P} \Big _T$		$+ \frac{\partial \epsilon_{IR}}{\partial P} \Big _T$
Parallel				
Quartz	-39.60	33.39	a	-72.99
Sapphire	-120.8	-3.87	b	-116.9
Calcite	564.1	13.08	c	551.0
Magnesium fluoride				
	-76.23	(7)	d	(-83)
Perpendicular				
Quartz	68.48
Sapphire	-85.31	-3.54	b	-81.77
Calcite	109.1	16.58	c	92.48
Magnesium fluoride				
	-91.52	(7)	d	(-99)

^aReference 7.

^bReference 9.

^cReference 8.

^dE. D. Schmidt and K. Vedam, J. Phys. Chem. Solids 27, 1573 (1966). (Results for calcium fluoride.)

$$\frac{\epsilon_{\parallel}}{(\epsilon_{\parallel})_{P=0}} = \frac{(1 + a_{\parallel} P + b_{\parallel} P^2)(1 - d_{\parallel} P + e_{\parallel} P^2)}{(1 - d_{\parallel} P + e_{\parallel} P^2)^2} \quad (10)$$

and

$$\frac{\epsilon_{\perp}}{(\epsilon_{\perp})_{P=0}} = \frac{1 + a_{\perp} P + b_{\perp} P^2}{1 - d_{\perp} P + e_{\perp} P^2} \quad (11)$$

Consequently, values of the dielectric constant at all pressures from 0 to 0.3 GPa can be generated using Eqs. (10) and (11) and the data listed in the present work.

III. DISCUSSION

A. Infrared contribution

For most of the samples of the present work, the predominant contributions to the low-frequency dielectric constant are electronic and ionic. For quartz perpendicular to the optic axis, however, there is a piezoelectric contribution.⁸ Because of the lack of information on the effect of pressure on the piezoelectric contribution, quartz perpendicular to the optic axis will not be considered further in this paper. For the other materials, then, the following equation is applicable:

$$\epsilon = \epsilon_{el} + \epsilon_{IR} \quad (12)$$

where ϵ_{el} is the electronic contribution and is equal to the square of the refractive index, and ϵ_{IR} is the ionic contribution. The effect of pressure on the refractive index has been reported for three of the materials in this report.⁹⁻¹¹ In addition, the value for magnesium fluoride has been approximated by using the value for calcium fluoride.¹² Since the pressure derivative of the dielectric constant can be written as

$$\frac{\partial \epsilon}{\partial P} \Big|_T = \frac{\partial \epsilon_{el}}{\partial P} \Big|_T + \frac{\partial \epsilon_{IR}}{\partial P} \Big|_T \quad (13)$$

the effect of pressure on the infrared contribution to the dielectric constant can be determined. The three components of Eq. (13) are listed in Table VI. It is seen that five of the

TABLE VII. Basic data used in the calculations.

Sample	$\epsilon_{el}^{\parallel}$	ϵ_{el}^{\perp}	χ_T ($10^{-12}/\text{Pa}$)	β ($10^{-6}/\text{K}$)
Quartz	2.41 ^a	...	2.69 ^c	35.1 ⁱ
Sapphire	3.10 ^b	3.13 ^b	3.97 ^f	15.9 ^j
Calcite	2.21 ^c	2.75 ^c	13.7 ^g	14.6 ^k
Magnesium fluoride				
	1.9 ^d	1.9 ^d	11.5 ^h	31.2 ^l

^aReference 7.

^bI. H. Malitson, J. Opt. Soc. Am. 52, 1377 (1962).

^cReference 8.

^dA. S. Barker, Jr., Phys. Rev. A 136, 1290 (1964).

^eH. J. McSkimin, P. Andreatch, Jr., and R. N. Thurston, J. Appl. Phys. 36, 1624 (1965).

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^gD. P. Dandekar, J. Appl. Phys. 39, 3694 (1968); Phys. Rev. 172, 873 (1968).

^hH. R. Cutler, J. J. Gibson, and K. A. McCarthy, Solid State Commun. 6, 431 (1968).

ⁱG. K. White, Cryogenics 4, 2 (1964).

^jB. Yates, R. F. Cooper, and A. F. Pojur, J. Phys. C 5, 1046 (1972).

^kReference 11.

^lJ. S. Browder, J. Phys. Chem. Solids 36, 193 (1975).

seven derivatives are negative.

In order to understand the reason for the sign of the derivatives, it is useful to separate the dielectric constant derivative into contributions from the infrared polarizability α_{IR} and the number of polarizable entities per unit volume N . In order to do this, the following analogy with the Clausius-Mosotti relation is useful:

$$(\epsilon_{IR} - 1)/(\epsilon_{IR} + 2) = KN\alpha_{IR} \quad (14)$$

where K is assumed to be a constant. Consequently, it follows that

$$\frac{3}{(\epsilon_{IR} - 1)(\epsilon_{IR} + 2)} \frac{\partial \epsilon_{IR}}{\partial P} \Big|_T = \chi_T + \frac{1}{\alpha_{IR}} \frac{\partial \alpha_{IR}}{\partial P} \Big|_T \quad (15)$$

where χ_T is the isothermal compressibility. The basic data used in the calculation are listed in Table VII, and the results are given in Table VIII.

It is found that six of the seven pressure derivatives of the infrared polarizability are negative. This implies that for those six materials, the effect of pressure is to inhibit the ionic motion, which is responsible for the infrared polariza-

TABLE VIII. Contributions to the pressure derivative of the ionic contribution to the dielectric constant (units are 10^{-12} Pa^{-1}).

Sample	$\frac{3}{(\epsilon_{IR} - 1)(\epsilon_{IR} + 2)} \frac{\partial \epsilon_{IR}}{\partial P}$	$= \chi_T + \frac{1}{\alpha_{IR}} \frac{\partial \alpha_{IR}}{\partial P}$
Parallel		
Quartz	-47.20	2.69
Sapphire	-4.46	3.97
Calcite	40.5	13.7
Magnesium fluoride		
	-27.1	11.5
Perpendicular		
Sapphire	-5.63	3.97
Calcite	6.82	13.7
Magnesium fluoride		
	-20.4	11.5

TABLE IX. Contributions to the temperature derivative of the dielectric constant (units are 10^{-4} K^{-1}).

Sample	$\left. \frac{\partial \epsilon}{\partial T} \right _V$	$= \left. \frac{\partial \epsilon}{\partial T} \right _P$	$+ \frac{\beta}{\chi} \left. \frac{\partial \epsilon}{\partial P} \right _T$
Parallel			
Quartz	-4.63	0.53	-5.16
Sapphire	10.55	15.38	-4.83
Calcite	36.96	30.95	6.01
Magnesium fluoride	7.43	9.50	-2.07
Perpendicular			
Sapphire	5.09	8.51	-3.42
Calcite	28.31	27.15	1.16
Magnesium fluoride	6.33	8.81	-2.48

bility. Of particular interest is the rather large negative value for quartz.

For calcite parallel to the optic axis, however, the derivative is found to be positive. Consequently, for calcite, the application of pressure enables some ions, at least, to polarize more easily along the optic axis. For example, one possibility is that with the application of pressure, the carbonate ions rotate about the direction of the optic axis (which is perpendicular to their plane) thus facilitating motion of the calcium ions along the optic axis. Perhaps the distortions resulting from the anisotropic compressibility of the material are responsible for this effect. Certainly large distortions do occur because the linear compressibility parallel to the optic axis is almost four times that perpendicular to the optic axis. Also, anomalies in other properties for calcite are well established since the thermal expansion coefficient perpendicular to the optic axis is negative ($-5.5 \times 10^{-6}/\text{K}$ at 300 K) while it is positive parallel to the axis ($25.6 \times 10^{-6}/\text{K}$ at 300 K).¹³ It will, however, be of interest to investigate the reason for the dielectric anomaly.

B. Volume independent temperature effect

The results of the present work along with those of Ref. 1 allow a determination of the volume-independent temperature derivative:

$$\left. \frac{\partial \epsilon}{\partial T} \right|_V = \left. \frac{\partial \epsilon}{\partial T} \right|_P + \frac{\beta}{\chi_T} \left. \frac{\partial \epsilon}{\partial P} \right|_T, \quad (16)$$

where β is the volume thermal expansion coefficient. The isobaric temperature derivative at 300 K was determined from the results of Ref. 1 and those results along with the volume independent temperature derivative are listed in Table IX. Also, it follows that

$$\left. \frac{\partial \epsilon}{\partial T} \right|_V \approx \left. \frac{\partial \epsilon_{\text{IR}}}{\partial T} \right|_V, \quad (17)$$

since the effect of temperature on the refractive index at constant volume is usually quite small.

It is seen that all values of the volume-independent temperature derivative are positive except for quartz. It has been

shown¹⁴ that these values reflect the anharmonic self-energies for the materials. In particular, it is shown that whether the quantity is positive or negative in large part reflects the dominance of the cubic or quartic terms, respectively, in the lattice potential energy. Thus the cubic terms are dominant for calcite, sapphire, and magnesium fluoride, while for quartz the quartic term is dominant.

It would be of interest to investigate the reasons for the latter behavior.

IV. SUMMARY

In summary, then, the low-frequency dielectric constant for quartz, sapphire, calcite, and magnesium fluoride has been measured both parallel and perpendicular to the optic axis at several temperatures over the pressure range 0–0.3 GPa. The results, when compared with the reported values for the effect of pressure on the high-frequency dielectric constant, indicate that pressure decreases the infrared contribution to the dielectric constant for all materials except calcite. Consequently, the infrared polarizability decreases with pressure for all but calcite. Further, it is found that the infrared polarizability decreases with pressure for calcite perpendicular to the optic axis, but increases with pressure parallel to the optic axis. In addition, it is shown that the volume-independent temperature derivative of the low-frequency dielectric constant is positive for sapphire, calcite, and magnesium fluoride showing the cubic terms in the lattice potential energy dominate, while for quartz, the derivative is negative, implying that quartic terms are dominant.

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